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Analysis of multiple mycotoxins in cereals under ambient conditions using direct analysis in real time (DART) ionization coupled to high resolution mass spectrometry

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<http://dx.doi.org/10.1016/j.talanta.2010.08.029>

Direct analysis in real time (DART) ionization coupled to an (ultra)high resolution mass spectrometer based on orbitrap technology (orbitrapMS) was used for rapid quantitative analysis of multiple mycotoxins isolated from wheat and maize by modified QuEChERS procedure. After initial evaluation of ionization efficiencies for major groups of mycotoxins achievable with DART technology, sample preparation procedure and instrument parameter settings were optimized to obtain sensitive and accurate determination of most intensively ionizing toxins (deoxynivalenol, nivalenol, zearalenon, acetyldeoxynivalenol, deepoxy-deoxynivalenol, fusarenon-X, altenuene, alternariol, alternariolmethylether, diacetoxyscirpenol, sterigmatocystin). The lowest calibration levels (LCLs) estimated for the respective analytes ranged from 50 to 150 $\mu\text{g kg}^{-1}$. Quantitative analysis was performed either with the use of matrix-matched standards or by employing commercially available ^{13}C -labeled internal standards (available for deoxynivalenol, nivalenol and zearalenon). Good recoveries (100-108%) and repeatabilities (RSD 5.4-6.9%) were obtained at spiking level 500 $\mu\text{g kg}^{-1}$ with isotope dilution technique. Based on matrix-matched calibration, recoveries and repeatabilities were in the range 84-118% and 7.9-12.0% (RSD), respectively. The trueness of data obtained for deoxynivalenol and zearalenon in wheat/maize by DART-orbitrapMS was demonstrated by analysis of certified reference materials (CRMs). Good agreement of these results with data generated by validated ultra high pressure liquid chromatography-time-of-flight mass spectrometry method was documented.

Selective ionization of melamine in powdered milk by using argon direct analysis in real time (DART) mass spectrometry.

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Analyst. 2010 Apr;135(4):696-9. Epub 2010 Feb 5.

5-Hydroxymethylfurfural (5-HMF) is a compound with the elemental composition $\text{C}(6)\text{H}(6)\text{O}(3)$ that is present in powdered milk. Protonated 5-HMF (calculated m/z 127.0395) has the same nominal m/z as protonated melamine (calculated m/z 127.0732) and can interfere with direct analysis of melamine in powdered milk. Tandem mass spectrometry and high-resolution mass spectrometry have been previously used to distinguish melamine from 5-HMF. An alternative approach is presented here that uses the direct analysis in real time (DART) ion source operated with argon gas in combination with acetylacetone and pyridine reagent gases to selectively ionize melamine and eliminate the interference from 5-HMF. High-resolution/accurate mass data were used to verify the elimination of the 5-HMF interference and confirm the melamine elemental composition. With further refinement, this technique could lead to a rapid analysis method for screening large numbers of samples.

Rapid identification of additives in poly(vinyl chloride) lid gaskets by direct analysis in real time ionisation and single-quadrupole mass spectrometry

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Rapid Commun Mass Spectrom. Volume 24, Issue 1, pages 21–29, 15 January 2010

Gaskets for lids of glass jars usually consist of poly(vinyl chloride) (PVC) containing plasticisers and additional additives, which may migrate into packed foodstuffs. To conform to legal regulations, any such migration has to be determined analytically, which is a big challenge due to the huge chemical variety of additives in use. Therefore, a rapid screening method by means of direct analysis in real time mass spectrometry (DART-MS), using a single-quadrupole mass spectrometer, was developed. On introducing a plastisol sample into the DART interface, protonated molecules and ammonium adducts were obtained as the typical ionisation products of any additives present, and cleavages of ester bonds as typical fragmentation processes. Generally, additives present in the 1% range could be directly and easily identified if ion suppressive effects deriving from specific molecules did not occur. These effects could be avoided by analysing toluene extracts of plastisol samples, and this also improved the sensitivity. Using this method, it was possible to identify phthalates, fatty acid amides, tributyl O-acetylcitrate, dibutyl sebacate, bis(2-ethylhexyl) adipate, 1,2-diisononyl 1,2-cyclohexanedicarboxylate, and even more complex additives like acetylated mono- and diacylglycerides, epoxidised soybean oil, and polyadipates, with a limit of detection of $\leq 1\%$ in PVC plastisols. Only in the case of epoxidised linseed oil were levels of $\geq 5\%$ required for identification. The detection of azodicarbonamide, used as a foaming agent within the manufacturing process, was possible in principle, but was not highly reproducible due to the very low concentrations in plastisols.

Release kinetics of actives from chewing gums into saliva monitored by direct analysis in real time mass spectrometry.

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Rapid Commun Mass Spectrom. 2010 Apr 30;24(8):1165-71.

Direct analysis in real time mass spectrometry (DART-MS) was used to monitor the release kinetics of a taste-refreshing compound from chewing gums into the saliva of subjects. A new DART-MS sample probe was designed which was about four times more sensitive than the current benchmark probe. This decreased the impact of the dilution of the saliva samples that was required to minimize ion suppression effects and make quantitative analyses without an internal standard possible. The new probe was also about three times more reproducible, which allowed quantitative measurements to be conducted manually without requiring the enhanced precision provided by an automatic sample positioner. The accuracy of analyses performed by DART-MS was verified by comparing the results obtained from saliva samples analyzed both by DART-MS and by a more classical liquid chromatography/mass spectrometry (LC/MS) method. This investigation showed good agreement between the two techniques. DART-MS could then be used to objectively demonstrate the efficiency of a granular carbohydrate-based delivery system to boost for a few minutes the release of a lipophilic flavor raw material with a high octanol/water partition coefficient, cyclohexanecarboxamide, N-ethyl-5-methyl-2-(1-methylethyl) (WS-3), from chewing gum into saliva.

Applications of direct analysis in real time-mass spectrometry (DART-MS) in Allium chemistry. (Z)-butanethial S-oxide and 1-butenyl thiosulfinates and their S-(E)-1-butenylcysteine S-oxide precursor from Allium sicutum.

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J Agric Food Chem. 2010 Jan 27;58(2):1121-8.

Lachrymatory (Z)-butanethial S-oxide along with several 1-butenyl thiosulfinates was detected by DART mass spectrometry upon cutting Allium sicutum, a popular ornamental Allium species used in some cultures as a spice. (Z)-Butanethial S-oxide isolated from the plant was shown to be identical to a synthetic sample. Its likely precursor, (R(S),R(C),E)-S-(1-butenyl)cysteine S-oxide (homoisoalliin), was isolated from homogenates of A. sicutum, and a closely related species Allium tripedale, and fully characterized. Through use of LC-MS, a series of related gamma-glutamyl derivatives were tentatively identified in A. sicutum and A. tripedale homogenates, including gamma-glutamyl-(E)-S-(1-butenyl)cysteine and its S-oxide, gamma-glutamyl-S-butylcysteine and its S-oxide, and gamma-glutamyl-S-methylcysteine and its S-oxide. Because compounds containing the 1-butenyl group have not been previously identified in genus Allium species, this work extends the range of known Allium sulfur compounds. The general applicability of DART mass spectrometry in identifying naturally occurring, thermally fragile thial S-oxides and thiosulfinates is illustrated with onion, Allium cepa, as well as a plant from a different genus, Petiveria alliacea.

Profiling of Piper betle Linn. cultivars by direct analysis in real time mass spectrometric technique

Bajpai, V., Sharma, D., Kumar, B. and Madhusudanan, K. P.

Biomedical Chromatography, doi: 10.1002/bmc.1437

Piper betle Linn. is a traditional plant associated with the Asian and southeast Asian cultures. Its use is also recorded in folk medicines in these regions. Several of its medicinal properties have recently been proven. Phytochemical analysis showed the presence of mainly terpenes and phenols in betel leaves. These constituents vary in the different cultivars of Piper betle. In this paper we have attempted to profile eight locally available betel cultivars using the recently developed mass spectral ionization technique of direct analysis in real time (DART). Principal component analysis has also been employed to analyze the DART MS data of these betel cultivars. The results show that the cultivars of Piper betle could be differentiated using DART MS data.

Allium chemistry: Use of new instrumental techniques to “see” reactive organosulfur species formed upon crushing garlic and onion

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Pure Appl. Chem., 2010, Vol. 82, No. 3, pp. 535-539

Three different instrumental methods have been used to examine the organosulfur chemistry of intact and cut garlic and onions: X-ray fluorescence spectroscopic imaging (XFS), direct analysis in real time (DART) mass spectrometry, and ultra-performance liquid chromatography-(Ag⁺)-coordination ion spray mass spectrometry (UPLC-(Ag⁺)CIS-MS). The first technique has been used to map the location of different chemical forms of sulfur in intact and damaged onion cells, the second technique, to identify the reactive, volatile sulfur compounds formed on cutting the plants, and the third technique, to identify members of families of polysulfides found in the distilled oil of garlic.

Ambient mass spectrometry employing direct analysis in real time (DART) ion source for olive oil quality and authenticity assessment.

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Anal Chim Acta. 2009 Jul 10;645(1-2):56-63. Epub 2009 May 5.

A novel approach for the authentication of olive oil samples representing different quality grades has been developed. A new type of ion source, direct analysis in real time (DART), coupled to a high-resolution time-of-flight mass spectrometer (TOFMS) was employed for the comprehensive profiling of triacylglycerols (TAGs) and/or polar compounds extracted with a methanol-water mixture. The main parameters influencing the ionization efficiency of TAGs were the type of sample solvent, degree of sample dilution, ion beam temperature, and presence of a dopant (ammonia vapors). The ionization yield of polar compounds depended mainly on a content of water in the extract and ion beam temperature. Using DART-TOFMS, not only differentiation among extra virgin olive oil (EVOO), olive pomace oil (OPO) and olive oil (OO) could be easily achieved, but also EVOO adulteration with commonly used adulterant, hazelnut oil (HO), was feasible. Based on the linear discriminant analysis (LDA), the introduced method allowed detection of HO addition of 6 and 15% (v/v) when assessing DART-TOFMS mass profiles of polar compounds and TAGs, respectively.

Assessing direct analysis in real time-mass spectrometry (DART-MS) for the rapid identification of additives in food packaging

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Food Additives & Contaminants: Part A 2009.
26(12): p. 1611-1618.

The ambient ionization technique direct analysis in real time (DART) was characterized and evaluated for the screening of food packaging for the presence of packaging additives using a benchtop mass spectrometer (MS). Approximate optimum conditions were determined for 13 common food-packaging additives, including plasticizers, anti-oxidants, colorants, grease-proofers, and ultraviolet light stabilizers. Method sensitivity and linearity were evaluated using solutions and characterized polymer samples. Additionally, the response of a model additive (diethyl-hexyl-phthalate) was examined across a range of sample positions, DART, and MS conditions (temperature, voltage and helium flow). Under optimal conditions, molecular ion ($M+H^+$) was the major ion for most additives. Additive responses were highly sensitive to sample and DART source orientation, as well as to DART flow rates, temperatures, and MS inlet voltages, respectively. DART-MS response was neither consistently linear nor quantitative in this setting, and sensitivity varied by additive. All additives studied were rapidly identified in multiple food-packaging materials by DART-MS/MS, suggesting this technique can be used to screen food packaging rapidly. However, method sensitivity and quantitation requires further study and improvement.

Direct analysis of curcumin in turmeric by DART-MS.

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Phytochem Anal. 2009 Sep-Oct;20(5):372-7.

The new ion source technique, direct analysis in real time (DART) atmospheric pressure ionisation, allows high resolution mass measurements of gas, liquid and solid samples. As DART-MS produces $[M + H]^+$ molecular ions of most compounds, relatively simple and clear mass spectra are obtained even of multi-component samples. In order to take advantage of the capacity of DART-MS for the real time analysis of individual compounds in natural raw materials, a pilot study was performed using the well-known antioxidant botanical drug, turmeric.

OBJECTIVE: To establish the analysis methods of curcumin and its derivatives from various types of samples with DART-MS and compare the efficiency of the method with traditional HPLC method.

RESULTS: Different curcuminoids were successfully detected directly from the raw particles of *Curcuma longa*. When a turmeric extract was separated on a TLC plate, each band produced molecular ion peaks corresponding to curcumin, demethoxycurcumin and bisdemethoxycurcumin. Molecular ions of curcuminoids in turmeric-containing beverages and curry powder were also efficiently detected. In addition to high efficiency of qualitative analysis, the evaluation of its linearity showed that DART-MS can be applied for semi-quantitative determinations of curcumin over a large range (5-100 microg/mL).

CONCLUSION: A simple chemical profiling and semi-quantitative method for natural products using DART-MS might be applied to diverse field related quality control of medicinal plants or food ingredients.

Temperature-dependent release of volatile organic compounds of eucalypts by direct analysis in real time (DART) mass spectrometry.

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Rapid Commun Mass Spectrom. 2009 Aug;23(15):2241-6.

A method is described for the rapid identification of biogenic, volatile organic compounds (VOCs) emitted by plants, including the analysis of the temperature dependence of those emissions. Direct analysis in real time (DART) enabled ionization of VOCs from stem and leaf of several eucalyptus species including *E. cinerea*, *E. citriodora*, *E. nicholii* and *E. sideroxylon*. Plant tissues were placed directly in the gap between the DART ionization source skimmer and the capillary inlet of the time-of-flight (TOF) mass spectrometer. Temperature-dependent emission of VOCs was achieved by adjusting the temperature of the helium gas into the DART ionization source at 50, 100, 200 and 300 degrees C, which enabled direct evaporation of compounds, up to the onset of pyrolysis of plant fibres (i.e. cellulose and lignin). Accurate mass measurements facilitated by TOF mass spectrometry provided elemental compositions for the VOCs. A wide range of compounds was detected from simple organic compounds (i.e. methanol and acetone) to a series of monoterpenes (i.e. pinene, camphene, cymene, eucalyptol) common to many plant species, as well as several less abundant sesquiterpenes and flavonoids (i.e. naringenin, spathulenol, eucalyptin) with antioxidant and antimicrobial properties. The leaf and stem tissues for all four eucalypt species showed similar compounds. The relative abundances of methanol and ethanol were greater in stem wood than in leaf tissue suggesting that DART could be used to investigate the tissue-specific transport and emissions of VOCs.

Pro-inflammatory enzymes, cyclooxygenase 1, cyclooxygenase 2, and 5-lipoxygenase, inhibited by stabilized rice bran extracts.

Roschek B Jr, Fink RC, Li D, McMichael M, Tower CM, Smith RD, Alberte RS.
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J Med Food. 2009 Jun;12(3):615-23.

Rice bran, the outer bran and germ of the kernel and a by-product of rice milling, is rich in phytonutrients but has been underutilized because of lipid content instability. New methods for the processing of rice bran have yielded a stabilized form that is increasingly used in foods and dietary supplements. Recent studies have documented a role for stabilized rice bran (SRB) in treating diabetes and arthritis, although little is known of the bioactive compounds that impart these health benefits. Here we characterize the chemical composition of three extracts of SRB and identify the functional bioactives contributing to the inhibitory properties against three key pro-inflammatory enzymes (cyclooxygenase [COX] 1, COX2, and 5-lipoxygenase [5-LOX]) that control the inflammatory cascade involved in impaired joint health, pain, and arthritis. One extract (SRB-AI) demonstrated significant COX1 and COX2 inhibitory activities with 50% inhibitory concentration (IC(50)) values for COX1 and COX2 of 305 and 29 microg/mL, respectively, but no 5-LOX inhibition. The second extract (SRB-AII) inhibited COX1, COX2, and 5-LOX with IC(50) values of 310, 19, and 396 microg/mL, respectively. The third extract (SRB-AIII), a blend of SRB-AI and SRB-AIII, inhibited COX1, COX2, and 5-LOX with respective IC(50) values of 48, 11, and 197 microg/mL. Analysis of the extracts by direct analysis in real time time of flight-mass spectrometry revealed that SRB-AI, SRB-AII, and SRB-AIII contain over 620, 770, and 810 compounds, respectively. Of these, 17 were identified as key bioactives for COX and/or LOX inhibition. These SRB extracts have applications for functional foods and dietary supplements for control of inflammation and joint health.

Elderberry flavonoids bind to and prevent H1N1 infection in vitro.

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Phytochemistry. 2009 Jul;70(10):1255-61. Epub 2009 Aug 12.

A ionization technique in mass spectrometry called Direct Analysis in Real Time Mass Spectrometry (DART TOF-MS) coupled with a Direct Binding Assay was used to identify and characterize anti-viral components of an elderberry fruit (*Sambucus nigra* L.) extract without either derivatization or separation by standard chromatographic techniques. The elderberry extract inhibited Human Influenza A (H1N1) infection in vitro with an IC₅₀ value of 252±34 microg/mL. The Direct Binding Assay established that flavonoids from the elderberry extract bind to H1N1 virions and, when bound, block the ability of the viruses to infect host cells. Two compounds were identified, 5,7,3',4'-tetra-O-methylquercetin (1) and 5,7-dihydroxy-4-oxo-2-(3,4,5-trihydroxyphenyl)chroman-3-yl-3,4,5-trihydroxycyclohexanecarboxylate (2), as H1N1-bound chemical species. Compound 1 and dihydromyricetin (3), the corresponding 3-hydroxyflavonone of 2, were synthesized and shown to inhibit H1N1 infection in vitro by binding to H1N1 virions, blocking host cell entry and/or recognition. Compound 1 gave an IC₅₀ of 0.13 microg/mL (0.36 microM) for H1N1 infection inhibition, while dihydromyricetin (3) achieved an IC₅₀ of 2.8 microg/mL (8.7 microM). The H1N1 inhibition activities of the elderberry flavonoids compare favorably to the known anti-influenza activities of Oseltamivir (Tamiflu; 0.32 microM) and Amantadine (27 microM).

Identification of active ingredients in dietary supplements using non-destructive mass spectrometry and liquid chromatography-mass spectrometry

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Forensic Science International, 2009, 191, e5–e10.

A mid-forties woman purchased seven different dietary supplements from Thailand on the internet and subsequently died after taking these supplements. Since there were no ingredient labels on the supplements, we identified the active ingredients using direct analysis in real time-mass spectrometry (DART-MS), direct exposure probe-MS (DEP-MS), and liquid chromatography-MS (LC-MS). DART-MS gives exact molecular weights and DEP-MS shows the fragmentation of a molecule by electron ionization. Analyses using these two instruments are rapid and do not require extraction of the sample. The compounds predicted by DART-MS and DEP-MS were confirmed by LC-MS and the active ingredients of the seven dietary supplements were identified.

Control of Strobilurin Fungicides in Wheat Using Direct Analysis in Real Time Accurate Time-of-Flight and Desorption Electrospray Ionization Linear Ion Trap Mass Spectrometry

Schurek, J., Vaclavik, L.; Hooijerink, H.; Lacina, O.; Poustka, J.; Sharman, M.; Caldwell, M.; Nielsen, M. W. F.; Hajšlova, J.

Anal. Chem., 2008, 80 (24), pp 9567–9575

Ambient mass spectrometry has been used for the analysis of strobilurin residues in wheat. The use of this novel, challenging technique, employing a direct analysis in a real time (DART) ion-source coupled with a time-of-flight mass spectrometer (TOF MS) and a desorption electrospray ionization (DESI) source coupled with a linear ion trap tandem MS (LIT MSn), permitted a direct screen of the occurrence of target fungicides in treated grains in less than 1 min. For quantification purpose by DART-TOF MS, an ethyl acetate extract had to be prepared. With the use of a prochloraz as an internal standard, the performance characteristics obtained by repeated analyses of extract, spiked at 50 µg kg⁻¹ with six strobilurins (azoxystrobin, picoxystrobin, dimoxystrobin, kresoxim-methyl, pyraclostrobin, and trifloxystrobin), were in the following range: recoveries 78–92%, repeatability (RSD) 8–15%, linearity (R²) 0.9900–0.9978. The analysis of wheat with incurred strobilurin residues demonstrated good trueness of data generated by the DART-TOF MS method; the results were in a good agreement with those obtained by the conventional approach, i.e., by the QuEChERS sample handling procedure followed by identification/quantification employing high-performance liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). Tandem mass spectrometry using DESI-LIT MSn provided a sufficient number of product ions for confirmation of the identity of azoxystrobin and pyraclostrobin in incurred wheat samples.

Direct analysis in real time–time-of-flight mass spectrometry: Analysis of pesticide residues and environmental contaminants

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Chemicke Listy, 2008, 102(15), s324–s327.

DART–TOFMS technique can be used for determination of strobilurin fungicides in milled wheat grain extracts obtained by simple extraction procedure without time-consuming chromatographic separation. This method withstands the regulation demands of the European Union for the control of pesticide residues; moreover, simplified workflow enables examination of many samples within a short time period. Qualitative analysis of solid samples without any sample preparation is a challenging application of this novel technique. DART–TOFMS was shown to be a useful tool enabling rapid examination of plant surface and detection of pesticide used for flower treatment. Preliminary results indicate the potential to introduce new concepts into rapid screening of BFRs by employing DART–TOFMS. In addition, the information provided by both negative and positive mass spectra should be exploited with the aim to detect the presence of other contaminants.

Analysis of hairy root culture of Rauvolfia serpentina using direct analysis in real time mass spectrometric technique.

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Biomed Chromatogr. 2008 Jun;22(6):596-600.

The applicability of a new mass spectrometric technique, DART (direct analysis in real time) has been studied in the analysis of the hairy root culture of Rauvolfia serpentina. The intact hairy roots were analyzed by holding them in the gap between the DART source and the mass spectrometer for measurements. Two nitrogen-containing compounds, vomilenine and reserpine, were characterized from the analysis of the hairy roots almost instantaneously. The confirmation of the structures of the identified compounds was made through their accurate molecular formula determinations. This is the first report of the application of DART technique for the characterization of compounds that are expressed in the hairy root cultures of Rauvolfia serpentina. Moreover, this also constitutes the first report of expression of reserpine in the hairy root culture of Rauvolfia serpentina.

GC–TOF-MS and DART–TOF-MS: Challenges in the Analysis of Soft Drinks

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LCGC Europe Volume 21, Issue 5, 2008

The first case study involving the application of the head-space SPME–GC–TOF-MS combined with advanced data processing is a powerful tool to detect, identify, and automate the reporting trace peak of sensorically active taint compound present in soft drinks that would be "invisible" under the conditions commonly used, such as using GC coupled to conventional quadrupole or ion trap mass analysers. The second case study demonstrated the unique potential of a new ion source: direct analysis in real time (DART) coupled to a high-resolution time-of-flight-mass spectrometer (TOF-MS). The presence of a whole array of drink components could be detected and identified within a couple of seconds without any sample preparation. The distinguishing factors between two types of otherwise equally tasting soft drinks could be obtained on the basis of the proof of additives used. Further research aimed at obtaining performance characteristics such as limit of detection (LOD) and repeatability of measurement is currently being investigated.

Expression of tropane alkaloids in the hairy root culture of *Atropa acuminata* substantiated by DART mass spectrometric technique.

Banerjee S, Madhusudanan KP, Chattopadhyay SK, Rahman LU, Khanuja SP.
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Biomed Chromatogr. 2008 Aug;22(8):830-4.

Agrobacterium rhizogenes-mediated 'hairy root' cultures were established in *Atropa acuminata*. The chemical profiling of the hairy roots was carried out by a new mass spectrometric technique, direct analysis in real time (DART). The intact hairy roots were directly analyzed by holding them in the gap between the DART ion source and mass spectrometer. Two alkaloids, atropine and scopolamine, were characterized. The structural confirmation of the two alkaloids was made through their accurate molecular formula determinations. This is the first report of establishing hairy roots in *A. acuminata* as well as application of the DART technique for the chemical profiling of its hairy roots.

Pharmacokinetics of Cyanidin and Anti-Influenza Phytonutrients in an Elder Berry Extract Determined by LC-MS and DART TOF-MS

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Online J Pharmacol Pharmacokin, Volume 4: 1-17, 2008

Roschek B Jr, Alberte RS, Pharmacokinetics of Cyanidin and Anti-Influenza Phytonutrients in an Elder Berry Extract Determined by LC-MS and DART TOF-MS Online J Pharmacokinetics, 4: 1-17, 2008
Pharmacokinetic analyses were conducted on flavonoid phytonutrients in a Standardized Elder Berry Extract (SEBX) to determine bioavailability and uptake kinetics, and to compare LC-MS and DART TOF-MS for pharmacokinetic analyses. In the first study, serum and urine levels of Cyanidin from an SEBX lozenge were monitored by LC-MS in 6 individuals. In the second study, DART TOF-MS was used to compare the serum pharmacokinetics and bioavailability of Cyanidin and other flavonoids in SEBX when delivered as a slow-dissolve lozenge and as a drink from a single individual. When the SEBX lozenge was consumed, serum concentrations of Cyanidin were between 3.1 (LC-MS) and 5.4 nmol L⁻¹ (DART TOF-MS), equivalent to 2.7 and 4.7% bioavailability (BA), respectively. Averionol (methylated flavonoid) reached a C_{max} of 23 nmol L⁻¹ (10.5% BA), while Tristenonol (esterified flavonoid) and Istrocyanidin (A-type proanthocyanidin) reached C_{max} values of 3.9 nmol L⁻¹ (8.6% BA) and 7.5 nmol L⁻¹ (19.7% BA), respectively. When the SEBX was consumed as a drink, the bioavailability of Cyanidin decreased 20-fold (0.2% BA), while Averionol and Istrocyanidin decreased 2-fold (4.6 and 10.8% BA, respectively) compared to the lozenge ingestion, indicating primary uptake in the oral cavity. The bioavailability of Tristenonol increased by ca. 2-fold (18.8% BA) when the SEBX drink was consumed compared to the lozenge indicating the small intestine as the primary uptake site.

Rapid and unambiguous identification of melamine in contaminated pet food based on mass spectrometry with four degrees of confirmation.

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J Anal Toxicol. 2007 Jul-Aug;31(6):304-12.

A method for analyzing pet food without sample processing is described for rapid identification of melamine based on mass spectrometry (MS) using soft ionization by direct analysis in real time (DART) to provide accurate measurement of mass and isotope-peak intensities, in-source collisionally activated dissociation (CAD) fragmentation, and determination of active hydrogens. Usually, MS analyses based on other than electron ionization (EI) spectra can be suspect because of the limited amount of information provided by a single mass spectral peak (or very few peaks). In such cases, additional degrees of confirmation are desirable to increase confidence in the experimental results. Chromatographic retention time can provide a degree of confidence; however, this requires time and, in some cases, detailed sample processing. Currently, the United States Food and Drug Administration uses a gas chromatography-EI-MS technique for the determination of melamine in pet food that involves sample extraction and derivatization prior to a lengthy chromatographic separation. In the method described here, identification is also confirmed through a determination of the number of active hydrogen atoms in the analyte molecule achieved by hydrogen/deuterium (H/D) exchange by treatment with deuterium oxide (D₂O) at the initial stage of analysis. Cross-correlation of these four experimental data provides an unambiguous identification of melamine in contaminated pet food without the need for any sample preparation or chromatography. Limits of detection and the validity of the H/D exchange method as a confirmatory technique are also presented.

Direct mass spectrometric analysis of flavors and fragrances in real applications using DART.

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Rapid Commun Mass Spectrom. 2007;21(8):1361-6.

DART (Direct Analysis in Real Time) is an innovative technology to analyze complex solid samples at atmospheric pressure and ground potential by simply placing them between a DART ion source and a mass spectrometer. The analytes are ionized by a gun of neutral metastable species. The first examples of the application of DART to the analysis of flavor and fragrance raw materials in real, complex applications are reported here. A remarkably high potential of the technique is demonstrated. DART was applied to semi-quantitative analyses of perfumery raw materials deposited on smelling strips. In optimal cases, limits of detection around 100 pg were achieved. DART also allowed the assessment of the deposition and release of fragrance on surfaces such as fabric and hair. Finally, DART permitted the screening of twelve chewing gum samples for the possible presence of taste-refreshing compounds in less than 30 min.

Determination of isopropylthioxanthone (ITX) in milk, yoghurt and fat by HPTLC-FLD, HPTLC-ESI/MS and HPTLC-DART/MS.

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Anal Bioanal Chem. 2006 Jun;385(3):586-95.
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Two new HPTLC methods for quantification of isopropyl-9H-thioxanthen-9-one (ITX) in milk, yoghurt and fat samples have been developed. Extraction of ITX from milk and yoghurt was performed with a mixture of cyclohexane and ethyl acetate by employment of accelerated solvent extraction (ASE). For soy bean oil and margarine, a simple partitioning of ITX into acetonitrile was used. ITX and 2,4-diethyl-9H-thioxanthen-9-one (DTX) used as internal standard have been separated on silica gel 60 HPTLC plates with a mixture of toluene and n-hexane (4:1, v/v) and on RP18 HPTLC plates with a mixture of acetonitrile and water (9:1, v/v). Development was performed anti-parallel from both plate sides leading to a throughput of 36 separations in 7 min. Fluorescence measurement at 254/>400 nm was used for quantification. Limits of detection (S/N of 3) have been established to be 64 pg for ITX and DTX on both types of HPTLC plates. In fatty matrix (spiked butter) LOD of ITX was determined to be 1 µg kg⁻¹. In the working range monitored (20-200 µg kg⁻¹) polynomial regression of ITX showed a relative standard deviation (sdv) of +/- 1.51 % (r = 0.99981). Starting with the limit of quantification the response was linear (sdv = +/- 2.18 %, r = 0.99893). Regarding repeatability (n = 9) a coefficient of variation (CV) of 1.1 % was obtained for ITX at 32 ng on silica gel plates and of 2.9 % on reversed-phase plates. Repeatabilities (n = 4) of ITX determination at 20, 50 and 100 µg kg⁻¹ in milk, yoghurt, soybean oil and margarine showed CVs between +/-1.0 and 6.4 %. The results prove that modern planar chromatography is a rapid and cost-efficient alternative method to quantify ITX in milk-based or fatty matrices. Only positive results are confirmed by online ESI/MS in the SIM mode (LOQ 128 pg) and by DART/MS involving a minimal employment of the MS device, which is a

further advantage of HPTLC. Overall mean recovery rates of ITX at 20 or 50 and 100 µg kg⁻¹ (n = 8) were 41 % for milk, 70 % for yoghurt, 6 % for margarine and 12 % for soy bean oil. However, with the internal standard correction recoveries were about 130 % for milk and yoghurt and 70 and 97 % for margarine and soy bean oil, respectively.

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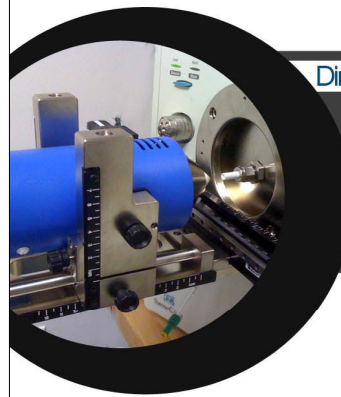
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